ANAEROBIC BIOREMEDIATION OF CHLORINATED SOLVENT SOURCE AREAS – WHAT CAN BE ACHIEVED?

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Introduction

Most common chlorinated solvents including tetrachloroethene (PCE), trichloroethene (TCE) and trichloroethane (TCA) are resistant to aerobic biodegradation but can be degraded through a process termed dehalorespiration where anaerobes use the chlorinated aliphatic hydrocarbon (CAH) as an electron acceptor for energy generation and cell growth. Early investigations indicated that high concentrations of dissolved CAHs inhibited biological activity and that biodegradation processes would be limited near dense non-aqueous phase liquids (DNAPLs). However, recent laboratory work has shown that some adapted cultures can rapidly and completely dechlorinate high concentrations of PCE to the non-toxic end-product ethene. This suggests that anaerobic bioremediation could be used to enhance DNAPL dissolution rates, speeding the cleanup of chlorinated solvent source areas.

A commonly proposed method for stimulating anaerobic biodegradation of a chlorinated solvent such as PCE would be to install a system of injection and recovery wells to circulate groundwater through the target zone. The groundwater would then be amended with a nutrient package including one or more dissolved organic substrates (lactate, molasses or other readily biodegradable, soluble material), inorganic nutrients (nitrogen and/or phosphorus) and possibly a source of trace vitamins and minerals. The organic substrates and other nutrients stimulate growth of dechlorinating microorganisms which convert PCE to TCE, DCE (dichloroethene), vinyl chloride (VC) and eventually to ethene. This process can potentially increase the PCE dissolution rate by reducing the aqueous PCE concentration, providing a larger concentration gradient to drive DNAPL dissolution.

In one of the first studies of biologically enhanced DNAPL removal, Carr et al. (2000) studied PCE removal in parallel biotic and abiotic continuous-flow stirred tank reactors (CFSTRs) containing a model NAPL consisting of PCE and tridecane. In the abiotic reactors, effluent concentrations were at the effective solubility of PCE indicating very rapid and efficient mass transfer between the NAPL and aqueous phases. In the biotic reactors, PCE was rapidly degraded to TCE and cis-DCE which was not degraded further. The conversion of less soluble PCE to the more soluble DCE resulted in a factor of 14 increase in PCE removal rates and reduced the time for removal of all chlorinated ethenes from the NAPL by a factor of 6. In a later study, Cope and Hughes (2001) examined biologically enhanced NAPL dissolution in upflow columns containing glass beads with a similar NAPL. Addition of pyruvate to dechlorinating columns resulted in a factor of 16 increase in PCE removal and a 5.0 to 6.5 times increase in chlorinated ethene removal in comparison with the abiotic, dissolution-only columns.

In contemporaneous studies, Yang and McCarty (2000) showed that anaerobic biodegradation could significantly enhance PCE dissolution. In a column containing residual PCE and fed pentanol, PCE was rapidly converted to DCE with some production of VC and ethene. Total ethene concentrations (PCE + TCE + DCE + VC + ethene) in the column effluent were 4 to 5 mM or about 5 times the aqueous solubility of PCE (0.9 mM), indicating a substantial increase in the effective PCE dissolution rate.

These laboratory studies clearly demonstrate that when NAPL dissolution is limited by chlorinated solvent solubility, biotransformation of less soluble PCE to more soluble DCE and other degradation products can significantly enhance PCE dissolution. However, at many field sites, DNAPL removal is often limited by both mass transfer rates and contaminant solubility. It is not clear whether conversion of PCE to DCE will have a significant impact on NAPL removal when PCE dissolution is mass transfer limited.

NAPL Dissolution-Biotransformation Model

To evaluate the potential for biological enhancement of NAPL dissolution at field sites, a simple mass transfer – biodegradation model was developed. TCE partitioning into the aqueous phase was described by the relationship

$$dC/dt = Km\ (Cs - C)$$

where C is the aqueous phase concentration, Cs is aqueous solubility, t is time, and Km is the effective NAPL-water mass transfer rate. Biotransformation of TCE to DCE to VC to ethene was modeled with constant first order transformation rates. Figure 1 shows simulated concentration distributions (with no biodegradation and enhanced

biodegradation) as groundwater flows past a 50 ft long pool of TCE and into the downgradient aquifer when mass transfer between the TCE pool and the aqueous phase is rapid. In the absence of biodegradation (Figure 1A), TCE concentrations rapidly increase up to the saturation limit (1100 mg/L) and then dissolution stops. With enhanced biodegradation (Figure 1B), the aqueous phase never becomes saturated with dissolved TCE increasing the net TCE dissolution rate. As TCE biodegradation rate (k) increases from 0 yr^{-1} to 365 yr^{-1}, the effective TCE dissolution rate increases by over a factor of four (Figure 1C). However TCE concentrations rarely approach the saturation limit at most field sites, suggesting that TCE dissolution is often limited by mass transfer rates, not by aqueous solubility.

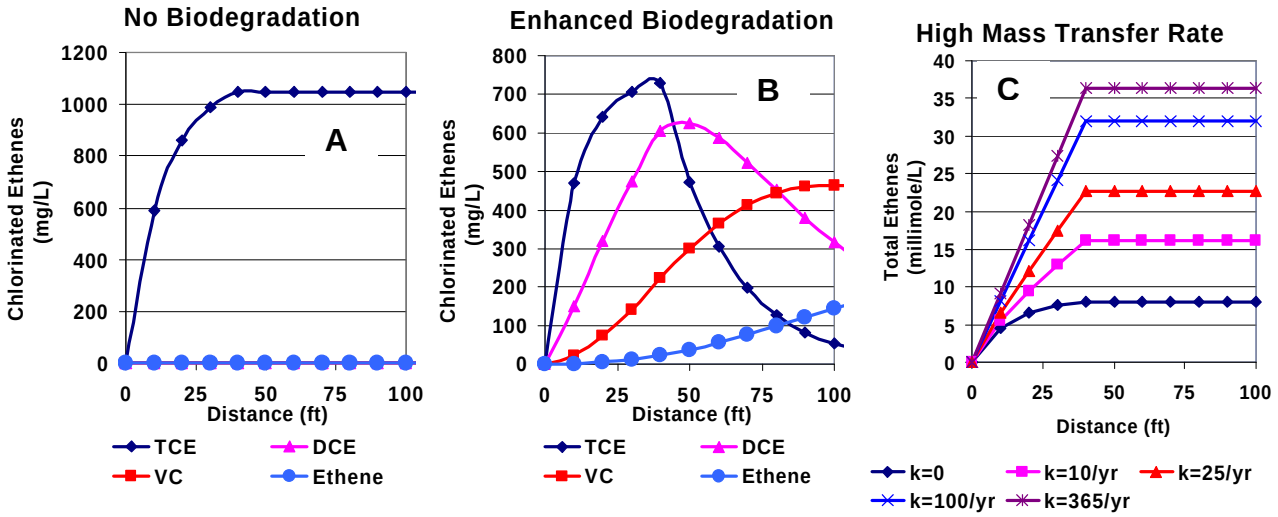

Figure 1 **Effect of degradation on TCE dissolution when mass transfer rates are high. Biotransformation processes maintain the TCE concentration well below solubility, substantially increasing the overall TCE removal rate.**

Figure 2 shows simulated concentration distributions when mass transfer between the TCE pool and the aqueous phase is slow. In the absence of biodegradation (Figure 2A), TCE concentrations slowly increase, reaching a maximum of 25 mg/L at the downgradient end of the 50 ft long TCE pool. With enhanced biodegradation (Figure 2B), dissolved TCE reaches a maximum of less than 10 mg/L at the downgradient end of the pool and then declines as TCE is converted to DCE, VC and ethene. However when mass transfer rates are limiting, increasing the TCE biotransformation rate from 0 yr^{-1} to 365 yr^{-1}, has essentially no effect on the TCE removal rate (Figure 1C) since TCE dissolution is not limited by TCE solubility.

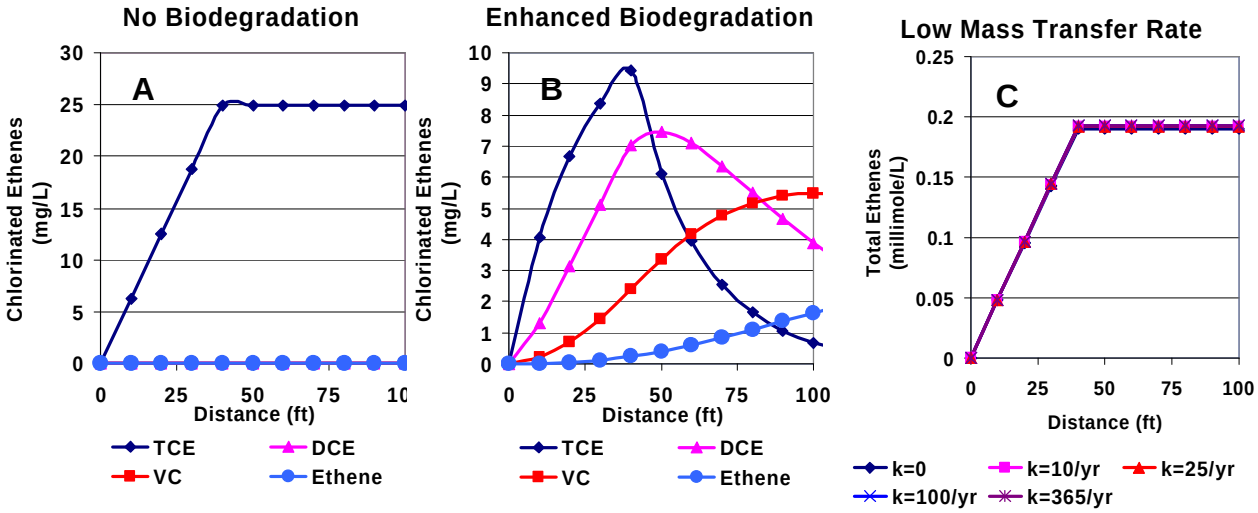

Figure 2 **Effect of degradation on TCE dissolution when mass transfer rates are low. Since TCE dissolution is not limited by solubility, converting TCE to DCE, VC and ethene has essentially no effect on the overall TCE removal rate.**

The situation in real aquifers is probably somewhere between the two extremes shown in Figures 1 and 2. At most sites, NAPL dissolution will be limited by both the contaminant aqueous solubility and the NAPL-water mass transfer rate. In any case, enhanced anaerobic bioremediation is not likely to be effective for rapid restoration of heavily contaminated source areas. Pump and treat systems are expected to take hundreds of years to restore these sites. In the most optimistic scenarios, enhanced anaerobic bioremediation with soluble substrates can increase the NAPL removal rate and reduce treatment time by a factor of five to ten.

Bioremediation for Source Area Containment

Anaerobic bioremediation can potentially be a very effective approach for reducing chlorinated solvent concentrations in the aqueous phase and preventing downgradient migration of dissolved contaminants. Sorenson et al. (1999) and Martin et al. (2001) have shown that injection of dissolved substrates can stimulate chlorinated solvent biodegradation in source areas, reducing the potential for downgradient migration. However, it is not clear whether this approach is removing a significant portion of the contaminant mass or just reducing dissolved concentrations. If the contaminant mass is not permanently removed, there will be a need for continual addition of biodegradable substrates.

Edible oil injection into source areas has been proposed as a low cost method for controlling downgradient migration of dissolved chlorinated solvents by: (1) reducing the effective permeability of the source area, reducing the groundwater flow velocity and dissolved contaminant mass flux; (2) reducing the effective solubility of contaminants in the aqueous phase; and (3) providing a slowly-degradable carbon source to support long-term plume containment. While this approach may have little impact on total mass of contaminants in the source area, it could significantly reduce the mass flux release from the source and the risk to downgradient receptors.

References

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